

Celsius;

cont  
B2

a temperature ranging from about 150 to about 600 degrees

an NH<sub>3</sub> gas flow of about 5 to about 1000 sccm;

an Ar gas flow of about 200 to about 2000 sccm;

an RF power ranging from about 50 to about 1000W;

a pressure ranging from about 1 millitorr to about 10 torr; and

a process time no greater than about 500 seconds.--

#### REMARKS

Claims 4-9 and newly added claims 76-88 are currently pending in the present application. In the Office Action mailed April 11, 2001, the Examiner rejected claims 4-7 under 35 U.S.C. § 102 (e) as being anticipated by United States Patent No. 6,165,802 to Cuchiario *et al.* (Cuchiario), and rejected claims 8-9 under 35 U.S.C. § 103(a) as being unpatentable over Cuchiario.

Applicant's invention exposes a conductive layer to an oxygen-inhibiting plasma prior to the formation of the another layer or layers on the conductive layer to substantially reduce the association of oxygen with the conductive layer during formation of the other layer or layers. By reducing the amount of oxygen associated with the conductive layer, the electrical characteristics of a semiconductor device including the conductive layer are improved, as will be discussed in more detail below with reference to the disclosed embodiments of the invention. The disclosed embodiments of the invention are discussed in comparison to the applied reference in order to help the Examiner appreciate certain distinctions between the pending claims and the subject matter of the applied reference. Specific distinctions between the pending claims and the applied reference will be discussed after the discussion of the disclosed embodiments and the applied reference. This discussion of the differences between the disclosed embodiments and applied reference does not define the scope or interpretation of any of the claims.

Figures 4 and 5 illustrate in-process semiconductor devices being formed by a process according to one embodiment of the present invention. As mentioned in the specification, for the purposes of explanation the in-process semiconductor device is assumed to

be a capacitor in the process of being constructed. In Figure 4, the capacitor includes a first conductive layer or 24, which may be formed from hemispherical silicon grain (HSG), formed over a substrate 22, and a dielectric 26 formed on the first conductive layer. In the examples of Figures 4 and 5, the dielectric 26 is formed from tantalum pentoxide  $Ta_2O_5$ . A second conductive layer 28 formed from tungsten nitride  $WN_x$  is then formed on the dielectric 26. The tungsten nitride layer 28 has a tendency to associate with oxygen, particularly if that layer is exposed to oxygen prior to a third conductive polysilicon layer 30 being formed on the tungsten nitride layer 28. During subsequent processing of the capacitor, the oxygen contained in the tungsten nitride layer 28 can combine with silicon from the polysilicon layer 30 to form an unwanted silicon dioxide layer 36 between the tungsten nitride layer 28 and the polysilicon layer 30. For example, a thermal process step such as the formation of a borophosphosilicate glass (BPSG) layer 34 over the polysilicon layer 30, which of course occurs after the formation of the polysilicon layer 30, may cause a reaction between the polysilicon layer 30 and the oxygen in the tungsten nitride layer 28 and thereby form the silicon dioxide layer 36.

Ideally, the HSG layer 24 forms a first plate of the capacitor, the tantalum pentoxide 26 forms the dielectric of the capacitor, and the tungsten nitride layer 28 and polysilicon layer 30 form the second plate of the capacitor. With the formation of silicon dioxide layer 36, however, the capacitor now includes a first capacitor corresponding to the HSG layer 24, tantalum pentoxide 26, and tungsten nitride layer 28, and a second capacitor in series with the first capacitor, with the second capacitor corresponding to the tungsten nitride layer 28, silicon dioxide layer 36, and polysilicon layer 30. These first and second capacitors connected in series have a combined capacitance that is less than that of the ideally formed capacitor. As will be understood by those skilled in the art, the thickness of the silicon dioxide layer 36 affects the value of the combined capacitance.

In the capacitor of Figure 4, the thickness of the silicon dioxide layer 36 is greatly reduced by exposing the tungsten nitride layer 28 to an oxygen-inhibiting agent prior to the formation of the polysilicon layer 30 to thereby greatly reduce the association of the tungsten nitride layer with oxygen. The silicon dioxide layer 36 in the embodiment of Figure 4 is less than 10 angstroms thick due to the oxygen-inhibiting agent, while in a conventional capacitor shown in Figure 3 the silicon dioxide layer 36 is about 10-40 angstroms thick. In the capacitor

of Figure 5, the exposure of the tungsten nitride layer 28 to the oxygen-inhibiting agent eliminates the formation of the silicon dioxide layer 36 altogether.

The oxygen-inhibiting agent may be an  $N_2$  and  $H_2$  plasma, with the tungsten nitride layer 28 ideally being exposed to this plasma prior to exposing tungsten nitride layer to an atmosphere associated with the formation of the polysilicon layer 30 or prior to exposing the tungsten nitride layer to oxygen. As described in the specification, it is believed the exposure of the tungsten nitride layer 28 to the  $N_2$  and  $H_2$  plasma or any of the other oxygen-inhibiting agents stuffs the tungsten nitride layer grain boundaries with nitrogen or otherwise passivates the tungsten nitride layer, making the bonds at the grain boundaries less active and less likely to associate with oxygen. It should be noted that even if the tungsten nitride layer 28 is exposed oxygen, the layer may thereafter be exposed to a reducing atmosphere, such as silane gas  $SiH_4$ , prior to formation of the polysilicon layer 30 to thereby reduce the oxygen content of the tungsten nitride layer 28 and reduce the thickness of any silicon dioxide layer 36 thereafter formed.

In another embodiment discussed with reference to Figure 6, a first conductive layer such as a tungsten nitride layer 128 is deposited over a substrate 122 and a dielectric layer 126, such as a tantalum pentoxide layer, is deposited over the tungsten nitride layer. In this situation, the deposition of the tantalum pentoxide layer 126 may cause the tungsten nitride layer 128 to incorporate oxygen, reducing the capacitance of a capacitor including the tungsten nitride layer and tantalum pentoxide layer. Accordingly, in this embodiment of the invention, the tungsten nitride layer 128 is exposed to a  $N_2$  and  $H_2$  plasma or other oxygen-inhibiting agent before depositing the tantalum pentoxide layer 126. As previously described, the  $N_2$  and  $H_2$  plasma passivates the tungsten nitride layer 128 to thereby prevent oxygen from being incorporated within the tungsten nitride layer.

Another embodiment of the present invention is discussed with reference to Figures 7-10 in which an interposing layer 52 such as a tungsten nitride layer 52 is formed between a conductive line material 48 to enhance the electrical contact between the line material and the plug, promote adhesion of the line material within a container 50, prevent or slow the diffusion of materials across the tungsten nitride layer boundary, or serve some other purpose. As previously described, the tungsten nitride layer 52 may associate with oxygen after it is

formed and subsequent thermal processes may result in the formation of an oxide layer 54 formed between the tungsten nitride layer 52 and the line material 48. Because the oxide layer 54 is an insulator, this layer will adversely affect the electrical connection between the line material 48 and the plug 46. By exposing the tungsten nitride layer 52 to an oxygen-inhibiting agent or a reducing atmosphere prior to formation of the line material 48, the thickness of the oxide layer 54 is reduced to a thickness of less than 10 angstroms or entirely eliminated as illustrated respectively in Figures 9 and 10. Thus, in all embodiments a conductive layer is exposed to an oxygen-inhibiting agent or reducing atmosphere prior to another layer being formed on the conductive layer to thereby reduce an ability of the conductive material to associate with oxygen.

The Cuchiario patent discloses a method of fabricating an integrated circuit that includes a ferroelectric element, such as a dielectric in a capacitor. Ferroelectric elements are utilized in forming capacitors that function as nonvolatile storage elements in nonvolatile integrated circuit memories. Referring to Figure 1, such a capacitor 118 includes a bottom electrode 120, a ferroelectric thin film 122 formed over the bottom electrode as the dielectric of the capacitor, and a top electrode 124 formed over the ferroelectric thin film. The electrical characteristics of ferroelectric thin film 122, such as high residual polarization, good coercive field, high fatigue resistance, and low leakage currents make them suitable for such applications. Cuchiario is particularly directed towards restoring the favorable electrical characteristics of the ferroelectric thin film 122 that are degraded during the step of hydrogen annealing that occurs as part of the formation of an integrated circuit including the capacitor 118 on a wafer 140. During the formation of a MOSFET 113 in the wafer 140, a silicon substrate 102 in which the MOSFET is formed experiences numerous defects in the single crystal structure of the substrate, which lead to the deterioration of the desired electrical characteristics of the MOSFET. These defects arise, for example, from such steps as ion implantation and high energy steps such as ion-mill and plasma etching.

Hydrogen annealing utilizes the reducing property of hydrogen to eliminate the defects in the silicon substrate 102, such as dangling bonds, and thereby restore the desired electrical characteristics of the MOSFET 113. Unfortunately, the use of hydrogen annealing in restoring the desired electrical characteristics of the substrate 102 and MOSFET 113 has the

unfortunate consequence of deteriorating the desired electrical properties of the ferroelectric thin film 122. This occurs due to the diffusion of hydrogen through the top electrode 124 and through the sides of the capacitor 118 to the ferroelectric thin film 122, which reduces the oxide contained in the ferroelectric thin film and has other negative affects on the desired electrical properties of the thin film.

Figure 2 in Cuchiaro is a flow diagram that illustrates a process for reversing the detrimental affects of hydrogen annealing on the ferroelectric thin film 122. This process will now be described with reference to Figures 1 and 2. In the process of Figure 2, steps 212-226 are the steps in which the bottom electrode 120 and ferroelectric thin film 122 are formed. Note that in step 226, which occurs prior to step 228 in which the top electrode 124 is formed, the ferroelectric thin film 122 is annealed in oxygen to form the desired ferroelectric thin film 122. After the ferroelectric thin film 122 is annealed in oxygen in step 226, the top electrode 124 is formed on the thin film in step 228 and a hydrogen barrier layer 126 (Figure 1) may then be formed over the top electrode 124 in step 230. The hydrogen barrier layer 126 inhibits the diffusion of hydrogen into the ferroelectric thin film 122 during subsequent hydrogen annealing of the wafer 140 (Figure 1) in step 232. The hydrogen annealing in step 232 may be performed using an  $H_2$  and  $N_2$  mixture as described in column 10, lines 43-45.

As previously described, the hydrogen annealing step 232 eliminates defects in the silicon substrate 102 such as dangling bonds and thereby restores the desired electrical characteristics of the MOSFET 113 but also detrimentally affects the electrical characteristics of the ferroelectric thin film 122 due to the diffusion of hydrogen into the ferroelectric thin film. In step 234, the wafer 140 is subjected to an oxygen-recovery anneal to restore the electrical properties of ferroelectric thin film 122 that were degraded due to the hydrogen annealing in step 232. The oxygen-recovery anneal and possibly other steps reverse the degradation of the electrical properties of the ferroelectric thin film 122 by reoxidizing chemical compounds in the ferroelectric thin film. *See* column 9, lines 5-17. The oxygen-recovery anneal of step 234 may be utilized to restore the desired electrical properties of the ferroelectric thin film 122 even with hydrogen barrier layer 126 is not formed over the top electrode 124. In Cuchiaro, it is the oxygen-recovery anneal and any other processing in step 234 that restores the desired electrical

properties of the ferroelectric thin film 122 and thereby allows the capacitor 118 to be utilized in nonvolatile memory applications.

In Cuchiaro, the hydrogen annealing step does not "expose" either the bottom electrode 120 nor the top electrode 124 to an oxygen-inhibiting agent as that term is used in present application. Cuchiaro does not disclose passivating either of the conductive electrodes 120, 124 by directly exposing the electrode to an oxygen-inhibiting agent or reducing atmosphere prior to another layer being formed on the electrode. Instead, in Cuchiaro after the bottom and top electrodes 120, 124 are completely formed, the resulting structure is hydrogen annealed to achieve the purpose of hydrogen annealing (*i.e.*, to correct defects in the underlying substrate 102 created during formation of the nonvolatile memory cell). Note that if the top electrode 124 includes multiple layers, all of these layers are formed prior to the hydrogen annealing, with no individual layer being passivated prior to the formation of the another layer thereon.

It should be noted that in Cuchiaro, prior to the hydrogen annealing in step 232, the bottom electrode 120, ferroelectric thin film 122, and top electrode 124 may be exposed to oxygen individually or in groups as the respective layers are formed, with one example being the annealing of the ferroelectric thin film 122 in oxygen as discussed above. Thus, if the bottom electrode 120 was, for example, tungsten nitride then this tungsten nitride layer could associate with oxygen during the oxygen annealing in step 232. Furthermore, it should be noted that none of the embodiments of Cuchiaro disclose or suggest passivating a conductive layer prior to the formation of another layer on that layer, including the test example described with reference to Figure 4 in which a thin film capacitor 400 is annealed in an H<sub>2</sub> and N<sub>2</sub> mixture, as discussed in column 10, lines 15-67. The capacitor 400 is annealed in the H<sub>2</sub> and N<sub>2</sub> mixture after a bottom electrode 420, ferroelectric thin film 422, and a top electrode layer 424 have been formed, as would actually occur when the capacitor is being formed in an actual device like the nonvolatile memory cell of Figure 1. Thus, if the top electrode layer 424 include were to include a tungsten nitride and polysilicon layer, then both these layers would be formed prior to the annealing of capacitor 400.

Amended claim 4 recites a method of passivating a conductive material that includes providing the conductive material that has an ability to associate with oxygen and

directly exposing the conductive material to a plasma to reduce the ability of the conductive material to associate with oxygen prior to forming another conductive material on the conductive material. Cuchiaro neither discloses nor suggests directly exposing a conductive material to a plasma to reduce the ability of the conductive material to associate with oxygen prior to forming a second conductive material on that conductive material. Dependent claims 5-9 ultimately depend from claim 4 and are therefore allowable for at least the same reasons as claim 4. Moreover, although the Examiner indicates the processes set forth in claims 8 and 9 are obvious in view of Cuchiaro as involving only routine skill in the art, as explained above Cuchiaro is not directed to passivating a conductive layer but is instead directed to solving an entirely different problem. The processes of claims 8 and 9 would therefore not be obvious to one skilled in the art in view of Cuchiaro since such process parameters passivate a conductive layer, which is entirely unrelated to the problem being solved in Cuchiaro. The combination of elements recited in claim 4 is therefore allowable.

New claim 76 recites a method of passivating a conductive layer including providing a tungsten nitride layer, providing a polysilicon layer on the tungsten nitride layer, and directly exposing the tungsten nitride layer to a plasma to passivate the tungsten nitride layer prior to formation of the polysilicon layer on the tungsten nitride layer. Cuchiaro does not disclose a tungsten nitride layer with a polysilicon layer thereon, nor does Cuchiaro disclose or suggest exposing the tungsten nitride layer to a plasma to passivate the tungsten nitride layer prior to formation of the polysilicon layer on the tungsten nitride layer. The combination of elements recited in claim 76 is therefore allowable.

New claim 81 recites a method of passivating a conductive layer including providing a first conductive plug, providing a first conductive layer on the plug, directly exposing the first conductive layer to a plasma to passivate the first conductive layer, and after exposing the first conductive layer to a plasma to passivate the first conductive layer, forming a second conductive layer on the first conductive layer. Cuchiaro neither discloses nor suggests forming a plug, forming a conductive layer on the plug, directly exposing the conductive layer to a plasma to passivate the layer, and thereafter forming another conductive layer on the passivated conductive layer. The combination of elements recited in claim 81 is therefore allowable.

Independent claims 4, 76, and 81 are allowable for the reasons set forth above with regard to each claim. The claims dependent on the independent claims are also allowable because of their dependency on the patentable independent claims, and because of the additional limitations added by the dependent claims.

Attached hereto is a marked-up version of the changes made to the claims by the current amendment. The attached page is captioned "Version with Markings to Show Changes Made".

The present patent application is in condition for allowance. Favorable consideration and a Notice of Allowance are respectfully requested. The Examiner is requested to contact the undersigned at the number listed below for a telephone interview if, upon consideration of this amendment, the Examiner determines any pending claims are not in condition for allowance.

Respectfully submitted,  
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PFR:asw

Enclosures:

Postcard  
Check  
Fee Transmittal Sheet (+ copy)  
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VERSION WITH MARKINGS TO SHOW CHANGES MADE

**In the claims:**

Claim 4 has been amended as follows:

4. (Amended) A method of passivating a conductive material, comprising:  
providing said conductive material, wherein said conductive material has an ability to associate with oxygen; and  
directly exposing said conductive material to a plasma to reduce the ability of the conductive material to associate with oxygen prior to forming another conductive material on the conductive material.